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Thermal stability of phase change materials used in latent heat energy storage systems: A review

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ABSTRACT

Successful utilization of the latent heat energy storage system depends considerably on the thermal reliability and stability of the phase change materials (PCMs) used. Thermal stability of phase change material can be established by measuring the thermo-physical properties of the PCM after a number of repeated thermal cycles. A comprehensive knowledge of thermal stability of the PCMs as functions of number of repeated thermal cycles is essential to ensure the long-term performance and economic feasibility of the latent heat storage systems. In this paper, a detailed review is reported for thermal stability of different groups of PCMs. The PCMs are categorized as organic (paraffins and non-paraffins), inorganic (salt hydrates and metallics) and eutectics (organic eutectics and inorganic eutectics). Further, a broad database of different PCMs is developed for which thermal cycling tests were carried out by different researchers and reported in the literature. Some conclusions are derived after critical evaluation of thermal stability of different groups of PCMs. This review will assist to identify the most reliable PCM to be used for a particular application of latent heat energy storage system.

Contents

1. Introduction

Successful application of intermittent sources of energy like solar energy depends to a large extent on the method of energy storage. Energy storage not only provides bridge between supply and demand but also improves the performance and reliability of the system. Thermal energy storage (TES) is one such technology

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which can substantially reduce the total energy consumption and conserve the indigenous fossil fuels. TES may involve only sensible heat storage (storing of energy by heating or cooling), latent heat storage (by melting or vaporizing or solidifying or liquefying) or a combination of both. Sensible heat storage method is most commonly used for solar energy applications. However, the major drawback of sensible heat storage unit is the larger volume requirement especially for small temperature swing. The latent heat storage system is a superior way of storing thermal energy. This is because of its high storage density and isothermal nature of the storage process. A comparison between latent and sensible heat storage shows that storage densities typically 5 to 10 times higher can be reached using latent heat storage units [1–4].

Latent heat storage can be accomplished through solid–liquid, liquid–gas, solid–gas and solid–solid phase transformations. However, solid–liquid and solid–solid phase transformations are of practical interest. Solid–gas and liquid–gas transitions are associated with higher latent heat of fusion. But the problem with them is their large volume changes on phase transition. This rules out their potential utility in thermal storage systems. Large changes in volume make the system complex and impractical.

The latent heat storage materials are commonly known as phase change materials (PCMs). The study of phase change materials was pioneered by Telkes and Raymond [5] in the 1940s. However, it did not receive much attention until the energy crisis of the late 1970s and early 1980s when it was extensively researched for use in different applications especially for solar heating systems [6–37]. Although research into latent heat storage for solar heating systems continues [38–41], enormous work has been carried out to explore the use of PCMs in other applications, specifically, building air conditioning [42–45], underfloor heating system [46–48], building envelope [49–51] refrigeration system [52], electronics cooling [53–55], waste heat recovery [56–58], textiles [59,60], preservation of food, milk [61,62] to name a few.

During the last four decades many phase change materials, with a wide range of melting/freezing point, have been identified and studied extensively. These materials include organic (e.g., paraffins, fatty acids), inorganic (e.g., salt hydrates, metallic) and eutectics (e.g., mixture of organic and/or inorganic materials). A classification of PCMs for solid–liquid phase transformation is given in Fig. 1. Each group of PCMs with their properties, advantages and limitations have been comprehensively reported in various literatures [3,4,30,63–70]. An attempt is made here to compile the same in a tabular form as shown in Table 1.

Even though latent heat storage is a better option than sensible heat storage, the practical use of it is limited. This is due to low thermal conductivity of PCM, variation in thermo-physical

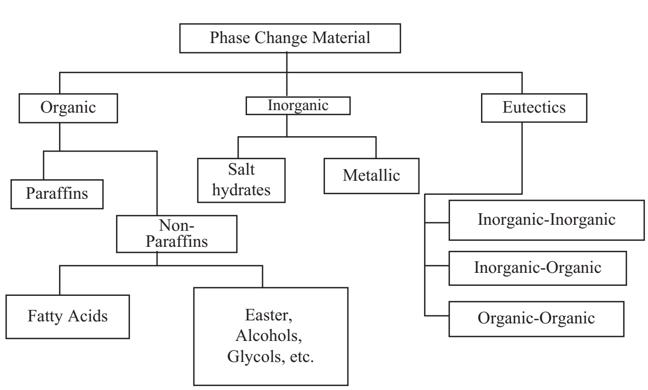


Fig. 1. Classification of PCMs [11].

Table 1
Comparison of different groups of PCMs [3, 4, 8–17].

	Organic material		Inorganic material		Eutectics
	Paraffins	**Non paraffins (fatty acids)**	**Salt hydrates**	**Mettalic**	
Formula	C_nH_{2n+2} (n=12–38)	$CH_3(CH_2)\cdot COOH$	$AB\cdot nH_2O$	–	–
Melting point	−12–71 °C	7.8–187 °C	11–120 °C	30–96 °C	4–93 °C
Heat of fusion	190–260 J/g	130–250 J/g	100–200 J/g	25–90 J/g	100–230 J/g
Features	1. Melting point and latent heat increases with chain length. 2. It is most used commercial PCM	1. Stearic acid melt over a wide range of temperature and have a large variation in latent heat of fusion	1. Oldest and most studied. 2. Its alloys of inorganic salts and water	1. Not seriously consider, due to weight penalty.	1. Composition of two or more components. 2. Melts and freeze without segregation
Cost	Expensive	Two to three times costly than paraffins	Low cost	Costly	Costly
Advantages	1. No tendency to segregate and to supercool. 2. Chemically stable. 3. High heat of fusion. 4. Compatible with all metal containers	1. Sharper phase transformation	1. Easy availability. 2. Sharpe melting point. 3. High thermal conductivity. 4. Low volume change than others. 5. Higher density	1. High heat of fusion per unit volume. 2. High conductivity	1. High heat of fusion per unit volume. 2. High conductivity.
Disadvantages	1. Low thermal conductivity. 2. Do not have sharp well-defined melting point. 3. Flammable 4. High volume change	1. Mildly corrosive 2. Flammable, should not exposed to excessively high temperature, flames or oxidizing agents.	1. Supercooling. 2. Corrosion on metal container. 3. Due to higher density, salts settles down at bottom and reduce active volume	1. Low heat of fusion per unit weight. 2. Low specific heat	1. Low heat of fusion per unit weight
Examples (melting pt. (°C), latent heat (J/g))	n-tridecane (4.5, 231), paraffin wax (32, 251), n-tricontane (65,252)	Acetic acid (16.7, 187), stearic acid (61, 200), lauric acid (42, 178), other non-paraffins as esters, glycol, i.e., glycerin (18, 198.7), bee wax (61.8, 177)	$CaCl_2\cdot 6H_2O$ (30, 170–192), $Na_2SO_4\cdot 10H_2O$ (32,251), $NaCl\cdot Na_2SO_4.6H_2O$ (18, 286), $MgSO_4\cdot 7H_2O$ (48.4, 200)	Gallium (30, 80.3), gallium–gallium (29.8,–), Bi–Pb–In eutectic (70, 29)	$Na_2SO_4+NaCL+KCl+H_2O$ (4, 234), $NH_2CONH_2+NH_4NO_3$ (46, 95)

properties under extended cycles, phase segregation, subcooling, incongruent melting, volume change and high cost. The feasibility of using phase change material in the latent heat storage system is based on desirable thermo-physical, kinetic, and chemical properties in addition to economic criteria [71]. The most important criteria that have limited widespread use of latent heat storages are the useful life of PCM-container systems. Insufficiently long-term use of PCMs is due to two factors: poor stability of the material properties and/or corrosion between the PCM and the container [2,64]. The present paper is aimed at critical review of thermal stability of different groups of low temperature PCMs. In addition, a broad database of different PCMs for which thermal cycling tests were carried out and reported in the literature is prepared. This review will help in the selection of reliable PCM for latent energy storage systems to be developed for particular applications.

2. Thermal stability of PCMs

In the last two decades, several reviewers have pointed out the importance of selection of PCMs on the basis of long-term stability of thermo-physical properties in their review papers [3,4,30,63–70]. Hasnain [63] emphasized that the selection of the PCM played important role in addition to heat transfer mechanisms for development of latent heat thermal energy storage system. He highlighted that the large-scale use of PCMs would require a thorough study of their thermo-physical properties in solid and liquid states. Zalba et al. [64] presented a critical review on a thermal energy storage system using PCMs from 237 sources. They listed over 150 materials being used as PCMs along with their thermo-physical properties. The authors pointed out the existence of large discrepancies in available data for the melting temperature and latent heat for the same PCMs. One of the conclusions made by them was that widespread usage of a latent heat storage was limited due to the insufficient long-term stability of storage materials.

Farid et al. [3] presented a review of the literature pertaining to the development of new class of phase change materials their applications to heating and cooling of buildings, thermal storage in satellites, protective clothing and new innovations in some other area. They highlighted the issues of separation, supercooling and stability of thermal properties of PCMs for long-term cycle processes. They concluded that melting point was the most important criterion for selecting a PCM for passive solar applications. Sharma and Sagara [65] compiled practical information on more than 250 PCMs. They also discussed the thermo-physical measurement techniques, thermal cycles and heat transfer enhancement techniques. They emphasized the need to study the effects of thermal cycling on melting point and latent heat of commercial grade PCMs. They presented a list of 15 PCMs on which thermal stability tests were carried out by different researchers.

Murat and Khamid [66] analyzed properties and applications of PCMs and suggested various methods of enhancing heat and mass transfer. They had provided thermo-physical properties of a series of PCMs. They indicated that information on temperature dependent heat capacity, thermal conductivity and density of materials in solid and liquid states was not widely available in open literature. One of the most significant conclusions made by them was that stability of thermal properties of PCMs should be tested for at least 1000 thermal cycles while developing commercial latent heat storage products.

The literatures reviewed above emphasize the fact that the economic feasibility of employing a PCM in a system depends on the life and cost of the storage material. Although the preparation, leakage, thermal conductivity and thermal storage properties of PCMs have been extensively studied, the reports on the thermal stability and/or reliability of PCMs are relatively inadequate [72]. The thermal stability test of PCMs should be carried out before using it in an actual application.

3. Thermal stability test

In order to ensure the long-term performance of the storage unit, the changes in the thermo-physical properties of prospective PCMs should be observed after repeated number of thermal cycles. A PCM is reliable if it is thermally, chemically and physically stable after a number of repeated thermal cycles. However, due to the inherent characteristics of these materials, PCMs may degrade over time. Large degradations of the thermo-physical properties over time are not desirable for any PCM.

Commercial grade PCMs are preferred for latent heat storage systems, due to their large scale availability and low cost. However, it has long been noted that the thermo-physical properties and behavior of commercial grade materials can vary from the values quoted in the literature. Therefore, the influence of a number of repeated thermal cycles on the melting temperature and latent heat of fusion in commercial grade PCMs must be evaluated, before the selection of a PCM for a particular application.

The most common application for PCM-based energy storage unit is solar applications. A solar thermal system with latent heat storage undergoes at least one melt/freeze thermal cycle per day. This can be considered as a normal cycle. However, a series of repeated, consistent thermal cycles can also be created in the laboratory, using an oven or an electric hot plate with a temperature controller. Such thermal cycle tests conducted under controlled conditions in the laboratory are called accelerated thermal cycle tests [73,74]. Small amount of material is withdrawn after each prescribed number of thermal cycles for obtaining the thermo-physical properties of PCMs. A PCM is thermally stable for latent heat storage applications if it undergoes negligible changes in the melting point and latent heat of fusion after repeated operative thermal cycles. Sharma et al. [74] have reported measured changes in the temperature-dependent properties of PCMs, such as the thermal conductivity, heat capacity and density after number of repeated thermal cycles.

3.1. Differential scanning calorimeter (DSC)

The most widely used technique in the laboratory to obtain melting temperature and heat of fusion of PCM samples is the differential scanning calorimeter (DSC). DSC techniques also include glass transitions, "cold" crystallization, phase change crystallization, product stability, cure/cure kinetics, and oxidative stability. DSC is a thermo-analytical technique in which the difference in the amount of heat required to increase the temperature of a sample and reference is measured as a function of temperature. Both the sample and reference are maintained at nearly the same temperature throughout the experiment. The reference sample should have a well-defined heat capacity over the range of temperatures to be scanned. The recommended reference material is alumina (Al_2O_3) for PCMs.

The basic principle of this technique is that when the sample undergoes a physical transformation such as phase transitions, in order to maintain both at the same temperature, more or less heat will require than the reference. The requirement of less or more heat flow to the sample depends on whether the process is exothermic or endothermic [75–77]. By observing the difference in heat flow between the sample and reference, differential

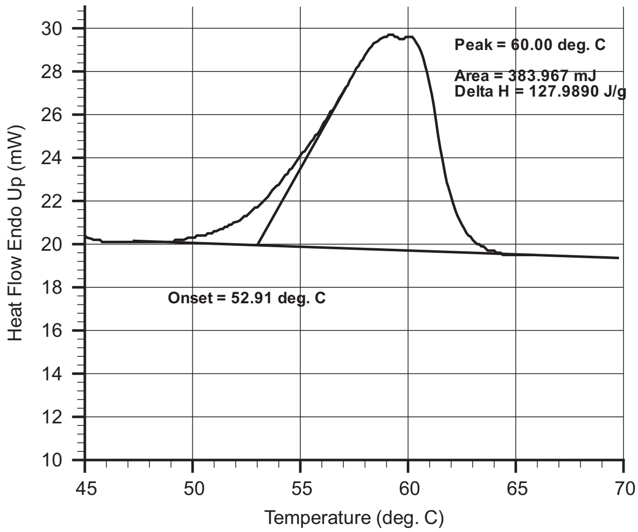


Fig. 2. DSC measurement of the latent heat of fusion and the melting temperature of paraffin [78].

scanning calorimeters are able to measure the amount of heat absorbed or released during such transitions. For obtaining the same, the plot between heat flow and temperature is then drawn. This is called the DSC curve. Latent heat of fusion is calculated using the area under the peak. The phase transition temperature is taken as the onset obtained by line fitting of the rising part of the peak. The phase transition range is calculated between onset temperature and temperature corresponding to the peak of the curve. A sample DSC curve [78] is shown in Fig. 2. It shows the DSC measurement of the latent heat of fusion and the melting temperature of paraffin. The quoted melting temperature range of paraffin is 58–60 °C. The obtained phase transition temperature range from DSC curve (Fig. 2) is 54.71–61.05 °C. The latent heat of fusion for paraffin obtained is 132.67 kJ/kg. In short, with the use of DSC, the thermo-physical properties of PCMs such as melting point, latent heat of fusion, specific heat, etc. are obtained. The observed changes in these properties after number of repeated thermal cycles can justify stability of the PCM.

A review of the literature on the thermal stability test PCMs carried out by various researchers on different groups of PCMs is discussed in the next section.

3.2. *Thermal stability test on organic PCMs*

Organic PCMs melt and freeze repeatedly without phase segregation (also called congruent melting). They crystallize with little or no supercooling (also called self-nucleation) and usually non-corrosiveness. Organic PCMs are further classified as paraffins and non-paraffins.

3.2.1. *Paraffins*

Paraffins have been widely used for the thermal energy storage due to their high heat of fusion, varied phase change temperatures, negligible supercooling, lower vapor pressure in a melt and chemically inert and stable behavior. They are also commercially available at reasonable cost. These PCMs are ecologically harmless and non-toxic [2,63,64]. Paraffins are easily available from many manufacturers. The normal paraffins of type C_nH_{2n+2} are the family of saturated hydrocarbons with almost similar properties. Higher the value of *n*, the higher is the melting temperature and latent heat of fusion [30]. Paraffin wax is the most commonly used commercial organic heat storage PCM [2]. It consists of mainly straight chain hydrocarbons having melting temperatures ranging between 23 and 67 °C.

Hadjieva et al. [79] considered three paraffins as samples A, B, and C with hydrocarbon formula $C_{22.2}H_{44.1}$ (m.p. 47.1 °C), $C_{23.2}H_{40.4}$ (m.p. 57.1 °C) and $C_{24.7}H_{51.3}$ (m.p. 62.6 °C), respectively. They studied the changes in thermo-physical properties after 900 thermal cycles of operation. They observed low enthalpy and broad phase transition range for sample C. They concluded that there was no noticeable degradation in the structure of paraffins A and B after 900 thermal cycles. However, paraffin of sample B was proposed as an efficient material because it showed highest enthalpy and it was a cheap by-product.

Sharma et al. [74] conducted 300 accelerated laboratory melt/freeze cycles of commercial-grade paraffin wax (m.p. 53 °C). They analyzed the changes in latent heat of fusion, melting temperature and specific heat using the DSC technique. In their study, paraffin wax was found to be more stable phase change material (PCM) after repeated thermal cycles. Later on, same authors [80] conducted 1500 accelerated thermal cycle test for the same paraffin wax by assuming a minimum life of the storage system as 5 years and 300 thermal cycles in a year. They concluded that paraffin showed stable behavior as compared to stearic acid. Shukla et al. [81] performed thermal cycling tests on three paraffin waxes of different melting temperatures indicated as type A (m.p. 58–60 °C), type B (m.p. 60–62 °C) and type C (m.p. 54 °C). For type A and type B paraffins, number of cycles of operation performed was 600 while type C was tested for 1500 cycles. The changes in melting point and latent heat with increasing in number of cycles were significant for type A and B. However, type C paraffin wax was found most suitable for latent heat storage purpose on the basis of its stability even after 1500 cycles of operation.

Alkan et al. [82] proposed novel form-stable paraffin/polypropylene (PP) composite for thermal energy storage application. In the composite, paraffin acted as a PCM and PP was used as supporting material. In order to determine thermal reliability of the form-stable material, 3000 accelerated thermal cycling tests were conducted. The changes in thermal properties and chemical stability of PCM after thermal cycling test was evaluated by DSC and Fourier transform infrared (FT-IR) spectroscopy. The results of DSC analysis indicated that the changes in melting point and latent heat of paraffin within the composites were quite low. Hence it was concluded that the prepared form-stable PCM had a good thermal reliability for the solar space heating application.

Sari et al. [83] focused on the preparation, characterization and thermal properties of microencapsulated *n*-heptadecane with polymethylmethacrylate shell. They investigated the chemical and thermal characterization of the microPCMs by using scanning electron microscope (SEM), DSC and thermo-gravimetric analysis (TGA). They observed that the microPCMs had good thermal reliability and chemical stability even after 5000 melt-freeze thermal cycles.

A list of paraffins mentioned so far is given in Table 2 along with their melting point and latent heat of fusion. It can be noted that the most studied paraffins have melting temperature in the range of 45 °C to 60 °C. These paraffins were tested for thermal stability up to 1500 thermal cycles. Further, it can also be noted that paraffins do not show regular degradation in its thermal properties after repeated number of thermal cycles.

3.2.2. *Non-paraffins*

Non-paraffins are the most abundant phase change materials with highly varying properties. These organic materials have further sub-groups of fatty acids and other non-paraffin organics like esters, alcohol, glycols, etc. However, fatty acids are most

Table 2
Melting point and latent heat of thermal cycled paraffins.

Sr. no.	PCMs	Melting point (°C)	Latent heat (J/g)	Thermal cycles	Reference
1.	Paraffin (70 wt%) + Polypropylene(30 wt%)	44.77	136.16	3000	Alkan et al. [82]
2.	Paraffin ($C_{22.2}H_{44.1}$) (technical grade)	47.1	166	900	Hadjieva et al. [79]
3.	Paraffin ($C_{23.2}H_{48.4}$) (technical grade)	57.1	220	900	Hadjieva et al. [79]
4.	Paraffin wax 53 (commercial grade)	53	184	300	Sharma et al. [74]
		53	184	1500	Sharma et al. [80]
5.	Paraffin wax 54	53.32	184.48	1500	Shukla et al. [81]
6.	Paraffin wax 58–60	58.27	129.8	600	Shukla et al. [81]
7.	Paraffin wax 60–62	57.78	129.7	600	Shukla et al. [81]
8.	*n*-Heptadecane/polymethyl methacrylate ($C_{17}H_{36}$)	18.4	84.7	5000	Sari et al. [83]

promising PCMs among all non-paraffins because of their availability in suitable phase change temperature and high heat of fusion. The fatty acids are easily producible from common vegetable and animal oils. Thus it provides an assurance of continuous supply despite the shortage of fuel sources [84–87]. In order to check the thermal stability of such PCMs, different researchers had carried out number of thermal cycling tests on these materials. The most common fatty acids which can be used as thermal storage materials are stearic acid, palmitic acid, lauric acid and myristric acid.

Abhat and Malatidis [88] determined the latent heat for palmitic (m.p. 61.2 °C) and lauric acid (m.p. 43.5 °C) after a short-term thermal period of 120 thermal cycles. They observed a small amount of supercooling during the freezing of fatty acids. This was insignificant enough to hamper their potential use as heat storage substances. Hasan and Sayigh [89] investigated myristic acid, palmitic acid and stearic acid with transition temperature 50–54 °C, 58–62 °C and 65–69 °C, respectively, for a domestic water heating system. They were industrial grade with 95% purity. They observed that the investigated fatty acids had exhibited at least 10% volumetric expansion when heated from room temperature to 80 °C. They observed that these PCMs loosen up to 10% of storage capacity (heat of fusion) after 450 thermal cycles (i.e., approx. 1 year).

Sharma et al. [74] conducted accelerated laboratory experiments to carry out DSC analysis for commercial grade stearic acid (m.p. 62.59 °C) and acetamide (m.p. 82.15 °C). The changes in latent heat of fusion, melting temperature and specific heat were observed. No loss due to evaporation was found even after 300 thermal cycles for each of these materials. Acetamide was found to be more stable. However, it absorbed moisture from the surroundings. Though stearic acid melted over a range of temperature, it was observed to be thermally stable after repeated melting/freezing cycles. For the same PCMs, 1500 accelerated thermal cycle tests were also conducted by Sharma et al. [80] to study the changes in latent heat of fusion and melting temperature. They concluded that acetamide had shown better stability as compared to stearic acid.

Sharma et al. [90] conducted accelerated thermal cycle test on urea (m.p. 133 °C) which could be used for solar cooker. Experimental results showed degradation in the thermal properties after first 50 thermal cycles only. Therefore, it was concluded that urea should not be used as latent heat storage material. Nikolic et al. [91] studied the solid/liquid transitions by DSC measurements in the fatty acid esters like methyl stearate (m.p. 37.8 °C) and methyl palmitate (m.p. 29 °C). More than 50 thermal cycles of the samples were carried out. They kept it in an atmospheric condition (at room temperature) for over 18 month period. The changes in thermal properties were not observed significantly.

Sari [85] carried out thermal reliability test on stearic acid (m.p. 54.7 °C), palmitic acid (m.p. 61.31 °C), myristic acid (m.p. 53 °C) and lauric acid (m.p. 42.46 °C) for 1200 melt/freeze cycles in order to measure the latent heat thermal energy storage (LHTES) characteristics. All the fatty acids used were industrial grade. Industrial grade PCM has a tendency to change its thermal behavior. He recommended that industrial grade PCM should be subjected to an accelerated thermal test before using it to the application. The investigated fatty acids had shown reasonably good thermal stability in view of the changes in latent heat of fusion and melting temperature with respect to thermal cycling.

Sari and Kaygusuz [92] studied thermal stabilities of industrial-grade (90–95% purity) fatty acids like stearic (m.p. 53.8 °C), palmitic (m.p. 59.9 °C), myristic (m.p. 53.8 °C) and lauric acid (m.p. 42.6 °C). DSC technique was used to determine latent heat storage capacity and the phase transition temperature of the PCMs after repeated thermal cycles such as 40, 410, 700 and 910. They observed that the thermal properties of stearic and lauric acid after 700 and 910 thermal cycles had reduced to an undesired level in actual latent heat storage utility. They concluded that the palmitic acids and myristic acids may be considered as suitable PCMs in the long-term solar thermal applications. They also studied the corrosion resistance of some construction materials to the fatty acids over a long period of exposure. The containment materials tested were stainless steel (SS 304L), carbon steel (Steel C20), aluminium (Al) and copper (Cu). From the gravimetric and metallographic corrosion test results, it can be concluded that stainless steel (SS 304L) with chromium oxide (Cr_2O) surface layer and aluminium (Al) metals with aluminium oxide (Al_2O_3) layer surface are essentially compatible with the investigated fatty acids. Carbon steel (Steel C20) and copper (Cu) metals as storage-container materials are preferentially compatible.

Shukla et al. [81] performed thermal cycling tests to check the stability of erythritol (m.p. 118 °C). Decrease in melting point and latent heat of fusion after 1000 thermal cycles were in the acceptable level. It was concluded that erythritol is a reasonably stable material. Sari and Karaipekli [86] prepared a novel form-stable PCM by incorporation of capric acid (CA) within the expanded perlite (EP) (m.p. 31.8 °C). EP is one of the most feasible options as an economical building material for incorporation of fatty acids as PCMs. EP is used in lightweight plasters and mortars, insulation, and ceiling tiles in the construction and manufacturing fields. Thermal reliability of the composite PCM for 1000, 3000 and 5000 cycles was evaluated using DSC analysis. They concluded that the form-stable composite PCM had shown good thermal reliability with respect to change in melting point and latent heat of fusion. Sari and Karaipekli [93] prepared another form-stable PCM for thermal energy storage and performed the thermal stability test. This form-stable PCM was a composite of palmitic acid (PA) and expanded graphite (EG) material (m.p. 60.88 °C). They performed 3000 thermal cycle test on this composite. In order to determine thermal and chemical stability of this composite PCM, DSC and FT-IR analysis were also

performed. The irregular changes in melting and freezing temperatures and latent heat of fusion were observed. However, these changes with increasing thermal cycling number were not significant in magnitude for LHTES applications. Therefore, it was concluded that the form-stable composite PCM had good thermal stability. FT-IR analysis showed no change in the shape and frequency values of all peaks before and after thermal cycles. This result indicated that the chemical structure of composite was also not affected by repeated number of thermal cycles.

The commercial grade acetanilide C_8H_9NO (m.p. 116 °C) was investigated to study the influence of number of melt/freeze cycles on melting point and latent heat of fusion by El-Sebaii et al. [97]. Acetanilide can be used as storage media inside the solar cookers. Negligible changes in melting point and latent heat of fusion were measured using the DSC technique after 500 thermal cycles. The compatibility of the PCM with the PCM containing materials like aluminum and stainless steel was also studied using the scanning electron microscope (SEM) after 500 cycles. Aluminum sample in contact with acetanilide showed nearly no corrosion. On the other hand, stainless steel samples showed very strong corrosion in contact with acetanilide. Therefore, it was recommended that acetanilide was a stable PCM with good compatibility with aluminum as a containing material after number of thermal cycles. They recommended acetanilide as a promising PCM for cooking indoors and during low-intensity solar radiation periods.

Table 3 provides a list of non-paraffins discussed so far along with their melting point and latent heat. Most studied non-paraffins investigated are palmitic acid, myristic acids stearic acid and lauric acid. Sari and Kaygusuz [92] concluded that the palmitic acids and myristic acids can be considered as better PCMs than most of the other fatty acids for long-term solar thermal applications. Palmitic acid has a higher latent heat than myristic acid.

3.3. Thermal stability test on inorganic PCMs

Inorganic materials are classified as salt hydrates and metallic PCMs.

3.3.1. Salt hydrates

Salt hydrates are attractive for heat storage applications because of their low cost and easy availability. They have a sharp melting point and higher thermal conductivity than others [64,65]. However, due to phase separation and supercooling of salt hydrates, researchers had given less attention to it. During the melting of salt hydrates, other hydrates or dehydrated salts are formed. They tend to settle out and reduce the active volume available for heat storage. This problem of phase separation can be eliminated to a certain extent by using gelled or thickened mixtures [26]. This process however influences the heat storage characteristics of the mixture and the mixture degrades with time [30]. Another major problem of salt hydrates is supercooling. It indicates that they do not start to crystallize at the specified freezing point. This can also be avoided using suitable nucleating agents to start the crystal growth in the storage media. The salt hydrates were used widely during the period between 1980 and 1990. The most salt hydrates were tested for thermal stability during this period.

Marks [19] investigated thermal stability of Glauber's salt for 320 thermal cycles. Borax ($Na_2B_4O_7 \cdot 10H_2O$) was used as nucleating agent and attapulgite clay was used as thickener. He performed calorimetric measurements on mixtures of Glauber's salt in order to compare the thermal energy storage capacity of the unthickened mixture to that of thickened one. The comparison was in terms of number of thermal cycles. The thermal capacity of the pure salt declined quickly from its initial value. This was also observed in thickened salt but it declined albeit slowly. He concluded that though the thickened material possesses a reproducible behavior upon thermal cycling, both the pure Glauber salt and the thickened mixture were unfit for long-term use as latent heat storage materials.

Wada et al. [37] investigated the decreasing heat storage capacity of sodium acetate trihydrate ($CH_3CO_2Na \cdot 3H_2O$) during thermal cycling. They performed calorimetric measurements on three kinds of samples viz., guaranteed grade sample, technical grade sample and technical grade sample, thickened with polyvinyl alcohol. The tests were carried out for 500 thermal cycles. Sodium pyrophosphate decahydrate ($Na_2P_4O_7 \cdot 10H_2O$) was used as nucleating agent. They concluded that the heat

Table 3
Melting point and latent heat of thermal cycled non-paraffins.

Sr. no.	PCM	Melting point (°C)	Latent heat (J/g)	Thermal cycles	Reference
1.	Acetamide (CH_3CONH_2)	82.15	262.78	300	Sharma et al. [74]
		82	263	1500	Sharma et al. [80]
2.	Acetanilide (C_8H_9NO)	113	169.4	500	El-Sebaii et al. [97]
3.	Capric acid (55 wt%)+expanded perlite (45 wt%)	31.80	98.12	5000	Sari and Karaipekli [86]
4.	Erythritol	117	339	1000	Shukla et al. [81]
5.	Lauric acid ($C_{11}H_{23}COOH$)	43.5	169.3	120	Abhat and Malatidis [88]
		42.46	176.6	1200	Sari [85]
		42.6	211.6	910	Sari and Kaygusuz [92]
6.	Methyl palmitate	29	215	50	Nikolic et al. [91]
7.	Methyl stearate	37.8	270	50	Nikolic et al. [91]
8.	Myristic acid ($C_{13}H_{27}COOH$)	50.4	189.4	450	Hasan and Sayigh [89]
		52.99	181.0	1200	Sari [85]
		53.8	192.0	910	Sari and Kaygusuz [92]
9.	Palmitic acid ($C_{15}H_{31}COOH$)	61.2	196.1	120	Abhat and Malatidis [88]
		57.8	201.2	450	Hasan and Sayigh [89]
		61.31	197.9	1200	Sari [85]
		59.9	197.9	910	Sari and Kaygusuz [92]
10.	Palmitic acid (80 wt%)+expanded graphite (20 wt%)	60.88	148.36	3000	Sari and Karaipekli [93]
11.	Stearic acid ($C_{17}H_{35}COOH$)	65.2	209.9	450	Hasan and Sayigh [89]
		62.59	154.63	300	Sharma et al. [74]
		54.7	159.3	1200	Sari [85]
		53.8	174.6	910	Sari and Kaygusuz [92]
		63	155	1500	Sharma et al. [80]
12.	Urea	133	250	50	Sharma et al. [90]

storage capacity of the technical grade sample decreased relatively slowly compared to that of guaranteed grade sample. They also reported that the performance of thickened material showed little deterioration during the thermal cycle test. Kimura and Kai [95] also checked thermal stability of sodium acetate trihydrate ($CH_3CO_2Na \cdot 3H_2O$) which was used by Wada et al. [37]. They used disodium phosphate (Na_2HPO_4) as nucleating catalyst. In order to verify whether excess water is effective or not for repeated thermal cycles, four samples were prepared by addition of excess water in the PCM, i.e., (i) $CH_3CO_2Na \cdot 3.02H_2O$, (ii) $CH_3CO_2Na \cdot 3.15H_2O$, (iii) $CH_3CO_2Na \cdot 3.30H_2O$ and (iv) $CH_3CO_2Na \cdot 3.60H_2O$. They observed phase separation after 100 thermal cycles for all four samples which solidified at about 50 °C. They also observed that the excess water had no significant influence on the improvement of phase change stability of this hydrate. They concluded that pure $CH_3CO_2Na \cdot 3H_2O$ cannot tolerate repeated phase change, unless settling of the anhydrous phase was avoided by a thickening agent. This conclusion drawn by them contradicts that by Wada et al. [37]. The amount of sample taken by Wada et al. [37] was too small (about 30 g) as compared to sample considered by Kimura and Kai [95] (220 g). This might be the reason for phase separation.

Calcium chloride hexahydrate ($CaCl_2 \cdot 6H_2O$) is the most well-known salt hydrates. Phase change stability of calcium chloride hexahydrate ($CaCl_2 \cdot 6H_2O$) with a slight excess of water was first investigated by Kimura and Kai [35]. The problem of phase separation is caused by the formation of $CaCl_2 \cdot 4H_2O$ during number of repeated thermal cycles. This $CaCl_2 \cdot 4H_2O$ tends to settle down at the bottom of the solution. $CaCl_2 \cdot 6H_2O$ decomposes continuously into $CaCl_2 \cdot 4H_2O$ with repeated thermal cycles. The calcium chloride hexahydrate ($CaCl_2 \cdot 6H_2O$) with a slight excess of water reduce the formation of $CaCl_2 \cdot 4H_2O$ through increasing its solubility. They found that NaCl had excellent nucleating ability for $CaCl_2 \cdot 6H_2O$. Thus they prepared and tested $CaCl_2 \cdot 6.11H_2O$: NaCl (1 wt%) for 1000 thermal cycles. They observed repeatability for phase change and no phase separation even after 1000 thermal cycles of operation for this PCM. Dissolved NaCl in $CaCl_2 \cdot 6H_2O$ crystal removed the requirement of adding a nucleating agent. Kimura and Kai [96] had also carried out 100 repeated thermal cycles for trichlorofluoromethane (R11) heptadecahydrate ($CCl_3F \cdot 17H_2O$) (m.p. 8.5 °C) as a heat storage material. Tetrabutyl ammonium fluoride hydrate ($(C_4H_9)_4NF \cdot 34.4H_2O$) was used as nucleating agent and polyacrylamide (PAA) was used as thickener. They found that freeze-thaw phase changes of $CCl_3F \cdot 17H_2O$–PAA gel was repeated successfully 100 times. They suggested that the $CCl_3F \cdot 17H_2O$–PAA gel would be a promising material for coolness storage.

Fellchenfeld et al. [97] studied the influence of thermal cycling on the heat of fusion of calcium chloride hexahydrate with the addition of the nucleating agent (strontium chloride hexahydrate) and the thickening agent (silica gel). They performed over 1000 thermal cycles of cooling and heating under laboratory conditions. This material had shown no deterioration in latent heat of fusion. Ting et al. [98] investigated the feasibility of fabricating durable PCM tube-sheets for effective latent heat storage device. They conducted thermal cycle tests of a latent heat storage unit having $Na_2SO_4 \cdot nH_2O$ as PCM and concluded that after 1000 accelerated cycles of charging and discharging tests, the tubes showed no sign of deterioration. However, they did not analyze the effect of thermal cycling on the thermo-physical properties of the PCM.

Porisini [99] had also studied the thermal performance stability of commercially available salt hydrates after 5650 thermal cycles. The considered salt hydrates were (i) Glauber's salt ($Na_2SO_4 \cdot 10H_2O$) (m.p. 32 °C), (ii) $CaCl_2 \cdot 6H_2O$ (m.p. 27 °C), (iii) $Na_2SO_4 \cdot 1/2NaCl \cdot 10H_2O$ (m.p. 20 °C), and (iv) $NaOH \cdot 3.5H_2O$ (m.p. 15 °C). The endothermic and exothermic peaks related to melting and solidification of $Na_2SO_4 \cdot 1/2NaCl \cdot 10H_2O$ and $NaOH \cdot 3.5H_2O$ had been observed to disappear after 300 and 10 thermal cycles, respectively. In the case of Glauber's salt, changes in the thermal properties were noticeable after 100 thermal cycles. He concluded that only the commercial $CaCl_2 \cdot 6H_2O$ showed a good thermal stability after 5650 thermal cycles. However, he did not analyze change in latent heat of melting and freezing.

Tyagi et al. [102] studied the changes in latent heat of fusion and melting temperature of calcium chloride hexahydrate ($CaCl_2 \cdot 6H_2O$) as a latent heat storage material after 1000 accelerated thermal cycle tests. They noticed that the $CaCl_2 \cdot 6H_2O$ melted between stable ranges of temperature and had shown small variations in the latent heat of fusion during the thermal cycling process. Thus, it can be a promising PCM for building heating and cooling applications. Shukla et al. [81] performed thermal cycling tests to check the stability of thermal energy storage systems for four selected inorganic phase change materials (PCMs), i.e., barium hydroxide, di-sodium tetraborate, sodium hydroxide and ferric nitrate. Barium hydroxide could not be melted even at very high temperature compared to what the melting temperature was quoted in the literature. In their experiments Di-sodium tetraborate and sodium hydroxide was observed to melt at temperature 4 °C higher than that was quoted in literature. These PCMs when subjected to a second thermal cycle remained solid even at 100 °C. Ferric nitrate did not get solidified even after keeping it for sufficient time. They finally concluded that none of the selected inorganic PCMs were useful for latent heat thermal energy storage purposes.

Sebaii et al. [94] investigated the influence of the melt/freeze fast cycling on melting point and latent heat of fusion of the commercial grade magnesium chloride hexahydrate $MgCl_2 \cdot 6H_2O$ (m.p. 116.7 °C). This PCM could be used as storage media inside solar cookers. The thermo-physical properties and compatibility with the containing material (aluminum and stainless steel) were studied using the DSC and SEM techniques respectively after 500 thermal cycles. They observed that $MgCl_2 \cdot 6H_2O$ in unsealed container was not stable (even with the extra water principle) due to phase segregation. In addition, it was not compatible with either aluminum or stainless steel. They did not recommend $MgCl_2 \cdot 6H_2O$ as a storage material inside solar cookers for cooking indoors. Further, same authors investigated changes in the thermo-physical properties of same magnesium chloride hexahydrate $MgCl_2 \cdot 6H_2O$ after 1000 thermal cycles [103]. In their work they used extra water and sealed the container (to prevent water evaporation from the PCM) in an attempt to avoid the segregation problem during melting of $MgCl_2 \cdot 6H_2O$. They found that PCM solidifies almost without supercooling except in a few cases where it showed maximum of 0.1–3.5 °C of supercooling. Here they concluded that the extra water and sealing of the container significantly improve the stability of $MgCl_2 \cdot 6H_2O$ against thermal cycling.

Table 4 provides a list of salt hydrates discussed so far along with their melting point and latent heat of fusion. It can be seen that calcium chloride hexahydrate is the most studied PCM for the melting range of 20–30 °C. Fig. 3 compares the latent heat of fusion per unit mass of various oraganic and inorganic PCMs undergoing a phase transition within the temperature range 0–120 °C. It is seen that almost all the PCMs which were undergoing the thermal cycle test are in the range of 20–60 °C except acetamide [74,80], acetanilide [97], trichlorofluoromethane heptadecahydrate [96], $MgCl_2 \cdot 6H_2O$ [94,103]. Most studied PCMs are in the range of 30–60 °C. This may be due to PCMs, which can be used for low temperature solar thermal applications like water heating, baking and drying should have a melting temperature in that range only. Further, it can be noted that PCMs have latent heat of fusion in the range of 120–225 kJ/kg.

Table 4
Melting point and latent heat of thermal cycled salt hydrates.

Sr. no.	PCMs	Melting point (°C)	Latent heat (J/g)	Thermal cycles	Reference
1.	Calcium chloride hexahydrate($CaCl_2 \cdot 6H_2O$)	29.8	190.8	1000	Kimura and Kai [35]
		28	86	1000	Fellchenfeld et al. [97]
		27	–	5650	Porisini [99]
		23.26	125.4	1000	Tyagi et al. [102]
2.	Glauber's salt ($Na_2SO_4 \cdot 10H_2O$)	32.4	238	320	Marks [19]
		32	–	5650	Porisini [99]
3.	Magnesium chloride hexahydrate ($MgCl_2 \cdot 6H_2O$)	111.5	155.11	500	Sebaii et al. [94]
		110.8	138	1000	Sebaii et al. [103]
4.	$Na_2SO_4 \cdot nH_2O$	–	–	1000	Ting et al. [39]
5.	$Na_2SO_4 \cdot 1/2NaCl \cdot 10H_2O$	20	–	5650	Porisini [99]
6.	$NaOH \cdot 3 \cdot 5H_2O$	15	–	5650	Porisini [99]
7.	Sodium acetate trihydrate ($NaCH_3COO \cdot 3H_2O$)	58	230	500	Wada et al. [37]
		58	252	100	Kimura and Kai [95]
8.	Trichlorofluoromethane heptadecahydrate ($CCl_3F \cdot 17H_2O$)	8.5	210	100	Kimura and Kai [96]

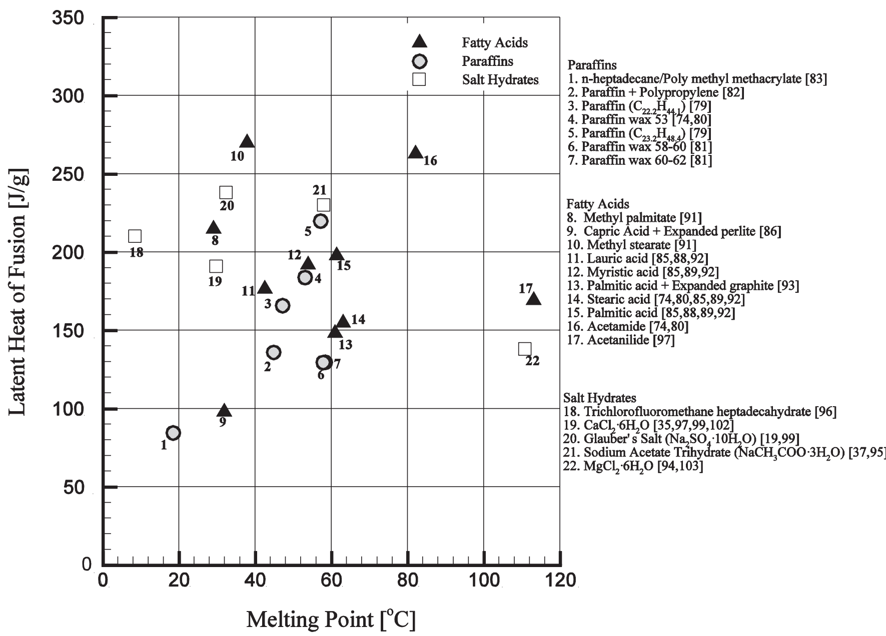


Fig. 3. Latent heat of fusion per unit mass of paraffins, fatty acids and salt hydrates undergoing a phase transition within the temperature range 0–120 °C.

Table 5
Melting point and latent heat of thermal cycled metallic.

Sr. no.	PCM	Melting point (°C)	Latent heat (J/g)	Thermal cycles	Reference
1.	Al–34%Mg–6%Zn alloy	454	314.4	1000	Sun et al. [55]

3.3.2. *Metallic PCMs*

This category includes the low melting metals and metal eutectics. Metallic PCMs have not yet been seriously considered for PCM technology because of weight penalties. However, when the compactness is important, they are likely candidates because of the high heat of fusion per unit volume. They have high conductivities. So fillers with added weight penalties are not required. As per authors' knowledge, till now the only single candidate of metallic category was investigated for thermal stability.

Sun et al. [114] determined the thermal stability and corrosion characteristics of the Al-34%Mg-6%Zn alloy when used as a latent heat energy storage material. The melting temperature and latent heat of fusion for this alloy are 454 °C and 314.4 kJ/kg. Thermal stability was checked for 1000 thermal cycles. The containment materials in the corrosion tests were stainless steel (SS 304L), carbon steel (Steel C20). The DSC results indicated that the change in melting temperature of the alloy was in the range of 3.06–5.3 °C and the latent heat of fusion decreased 10.98% after 1000 thermal cycles. The results showed that the investigated Al-34%Mg-6%Zn alloy had reasonably good thermal reliability as a latent heat energy storage material. Table 5 shows the details of the above-mentioned material.

3.4. *Thermal stability test on eutectics*

An eutectic is a minimum melting composition of two or more components, each of which melts and freezes congruently. During crystallization, a mixture of the component crystals is formed. They act as a single component. They freeze to an intimate mixture of crystals and melt simultaneously without separation

[104]. An eutectic PCM is a combination of two or more compounds of either organic, inorganic or both. The main problem with these compounds is the cost, actually some two or three times greater than organic or inorganic. A considerable number of eutectics may be tailored to almost any desired melting point for thermal energy storage systems. As the use of these materials is very new to thermal storage application, only limited data is available on thermo-physical properties. Therefore, the stability of the thermal properties of the new eutectics is needed to ensure the long-term performance of TES. Some of the organic–organic and inorganic–inorganic eutectics which were developed and checked for thermal stability by earlier investigators are discussed here.

3.4.1. Organic eutectics

Organic eutectics are the mixture of organic compounds. Investigations carried out on some of the organic eutectics whose phase change temperatures are suitable for low temperature energy storage unit are discussed in this section.

Feldman et al. [105] proposed a butyl stearate (BS)–gypsum board specimen which could be used as energy storage material for building. Butyl stearate (BS) was commercial mixture of 49% butyl stearate and 48% butyl palmitate. They conducted a thermal cycling test in a controlled temperature chamber for BS–gypsum board specimen. After number of thermal cycles, the melting point (17 °C) and freezing point (21 °C) of BS did not shift when incorporated in wallboard. The absorption and release of heat during the phase transition of the incorporated BS were not affected by its presence in gypsum.

Jotshi et al. [106] used ammonium alum/ammonium nitrate eutectic (melts at 53 °C and solidifies at 48 °C) for solar space heating applications and also conducted the thermal cycling for the same eutectic. At the end of 1100 thermal cycles, the enthalpy change value was found to be 5% lower than its initial value. Dimaano and Escoto [107] developed mixture of capric acid–lauric acid (CA 65 mol%–LA 35 mol%) as a possible phase change media for low thermal energy storage systems. The properties of different combinations of acids were verified with the use of DSC against existing data available in the literature. To confirm the long-term stability and reproducibility of the combination, 120 thermal cycles were carried out. Classical evaluation techniques were employed to determine the required thermodynamic, kinetic and other physical properties. In their experiments, no supercooling was observed. No significant change in volume took place and no material degradation was noted after number of thermal cycles.

Zhang et al. [84] studied the solid–liquid phase transitions in lauric acid, palmitic acid, stearic acid and their binary systems (LA–PA and LA–SA) by DSC and FT-IR. They noted that the fusion point of binary system was lower than that of single acid. They also investigated the stability of thermal properties of 22.95% LA–PA after 30, 50, 80, and 100 thermal cycles. They observed that the thermal properties of binary system were stable after 100 thermal cycles. They found binary systems of fatty acids as potential material for heat storage in solar energy applications. Eutectic mixtures of esters were prepared as thermal storage material by Nikolic et al. [91] to study thermal stability behavior. The composition of mixtures was methyl stearate (86 wt%)–methyl palmitate (14 wt%) (m.p. 23.9), methyl stearate (91 wt%)–cetyl palmitate (9 wt%) (m.p. 28.2) and methyl stearate (91 wt%)–cetyl stearate(9 wt%) (m.p. 22.2). Samples of commercial gypsum and bricks were immersed in selected molten materials and their thermal properties were also studied. The thermal cycles of the samples, kept in an air atmosphere and at room temperature over 18 month period, were checked occasionally. No changes in thermal properties were observed during more than 50 thermal cycles.

Sari et al. [108] carried out the study of latent heat storage characteristics of lauric acid–stearic acid (LA 75.5 wt%–SA 24.5 wt%), myristic acid–palmitic acid (MA 58 wt%–PA 42 wt%) and palmitic acid–stearic acid (PA 64.2 wt%–SA 35.8 wt%) eutectic mixtures for repeated thermal cycles. The eutectic mixtures were subjected to 360 repeated melt/freeze cycles. As the number of thermal cycles increased, the changes in the melting point and the latent heats of fusion of these materials were not regular, but were within reasonable level. It was concluded that the investigated eutectic mixtures of fatty acids used for passive solar thermal energy storage applications had shown reasonably good thermal reliability with respect to thermal cycling for about a 1 year of utility period. Sari [109] had determined latent heat storage characteristics of the other eutectic mixtures of lauric acid–myristic acid (LA 66 wt%–MA 34 wt%), lauric acid–palmitic acid (LA 69 wt%–PA 31 wt%), myristic acid–stearic acid (MA 64 wt%–SA 36 wt%). The tests were carried out using DSC after repeated melt/freeze cycles. They concluded that the studied PCMs have good thermal properties and thermal reliability for a 4-year energy storage period, which corresponds to 1460 thermal cycles.

Shilei et al. [110] conducted 360 accelerated thermal cycles to study the change in latent heat of fusion and melting temperature of phase change wallboards combined with the eutectic mixtures of capric acid–lauric acid (CA 65.12 wt%–LA 32.88 wt%). The same eutectic composition was also prepared by Dimaano and Escoto [107]. No regular degradation was found for 360 repeated thermal cycles. Hence they concluded that this phase change wallboard could be used for latent heat storage in HVAC system to reduce its scales and cost.

Karaipekli et al. [111] had prepared a novel form-stable phase PCM for building application. An eutectic mixture of capric acid–myristic acid (CA 73.5 wt%–MA 26.5 wt%) was confined in the porous expanded perlite (EP) by mass fraction 55%. It was ensured that there was no seepage for melted PCM from the composites. The mixture was described as form-stable. Thermal cycling test of the form-stable composite indicated better thermal stability in terms of changes in the thermal properties after 5000 thermal cycling. They found that the thermal conductivity of the form-stable CA–MA/EP composite was increased to about 58% by adding 10 wt% expanded graphite (EG). They considered the form-stable CA–MA/EP/EG composite PCM as an effective latent heat storage material in the building energy conservation due to suitable phase change temperatures, high latent capacities, good thermal reliability, and good thermal conductivity. Karaipekli et al. [87] focused on the preparation of another mixture of capric acid–stearic acid (CA 83 wt%–SA 17 wt%) as novel phase change material and determination of its thermal properties and thermal reliability by using DSC analysis technique. They showed that after 5000 accelerated thermal cycle test, the changes in phase change temperatures and the latent heats of the CA–SA mixture was irregular. They concluded that thermal properties and long-term thermal reliability of the prepared CA–SA mixture makes it potential phase change material for latent heat thermal energy storage system.

The latent heat storage characteristics of some fatty acid esters with glycerol had been investigated by Sari et al. [112]. The glycerol esters of some fatty acids viz., myristic, palmitic and stearic acid were prepared using the Fischer esterification method. The synthesized fatty acid esters were glycerol trimyristate (m.p. 31.96 °C), glycerol tripalmitate (m.p. 58.50 °C) and glycerol tristearate (m.p. 63.45 °C). From the DSC analysis, it was noticed that the synthesized PCMs had good thermal stability in terms of thermal properties after 1000 thermal cycles and no noticeable degradation was observed in the chemical structure of the esters. This means that the synthesized PCMs had good

thermal stability during a long utility period. Zuo et al. [113] conducted accelerated thermal cycles in order to determine the thermal stability of the caprylic acid/1-dodecanol binary system as cold storage material for air conditioning. After 60 and 120 thermal cycles, the melting temperature of the eutectic mixture had changed by −0.02 and −0.28 °C, and the latent heat of melting had changed by −0.17 and −3.1 J/g, respectively. The changes were in an acceptable level of a phase change material. Therefore, the caprylic acid/1-dodecanol eutectic mixture had good thermal stability.

3.4.2. Inorganic eutectics

Inorganic eutectics are the mixture of inorganic compounds. They are also well known as salt-based eutectics. Most of the inorganic eutectics are made from salt hydrates. Some of the inorganic eutectics whose thermal stability over the period of time was checked have been discussed here.

Kimura and Kai [95] investigated thermal stability of mixtures of $CH_3CO_2Na \cdot 3H_2O$ with $NaBr \cdot 2H_2O$ and $NaHCOO \cdot 3H_2O$ i.e., $NaCH_3COO \cdot 3H_2O$ (90 wt%)+$NaBr \cdot 2H_2O$ (10 wt%) and $NaCH_3COO \cdot 3H_2O$ (85 wt%)+$NaHCOO \cdot 3H_2O$ (15 wt%). These mixtures were found stable even after 1000 thermal cycles and shown no phase separation.

Kimura and Kai [100] studied mixture of $CaCl_2 \cdot 6H_2O$ with some salt hydrates [$CaBr_2 \cdot 6H_2O$, $Ca(NO_3)_2 \cdot 4H_2O$ and $Mg(NO_3)_2 \cdot 6H_2O$] or anhydrous nitrates (NH_4NO_3 and KNO_3). Such PCM is suitable for greenhouse purpose. Hence they prepared four samples: (i) $CaCl_2 \cdot 6H_2O$ (80 mol%)+$CaBr_2 \cdot 6H_2O$ (20 mol%), (ii) $CaCl_2 \cdot 6H_2O$ (93 wt%)+$Ca(NO_3)_2 \cdot 4H_2O$ (5 wt%)+$Mg(NO_3)_2 \cdot 6H_2O$ (2 wt%), (iii) $CaCl_2 \cdot 6H_2O$ (96 wt%)+NH_4NO_3 (2 wt%)+NH_4Br (2 wt%), and (iv) $CaCl_2 \cdot 6H_2O$ (96 wt%)+KNO_3 (2 wt%)+KBr (2 wt%). Barium fluoride was used as nucleating agent. They found no major degradation in melting point and latent heat of fusion of each mixture after 1000 thermal cycles.

Thermal characteristics of the mixture of magnesium nitrate hexahydrate ($Mg(NO_3)_2 \cdot 6H_2O$ (93 wt%)) and magnesium chloride hexahydrate ($MgCl_2 \cdot 6H_2O$ (7 wt%)) were investigated by Nagano et al. [101] for effective utilization of urban waste from the emerging generation system. The melting temperature of pure magnesium nitrate hexahydrate was about 90 °C. In order to use waste heat effectively, the melting point was needed to be brought down to 60 °C. They modulated the melting point by a mixture of magnesium nitrate hexahydrate and magnesium chloride hexahydrate. In order to check thermal stability and durability of the PCM, 1000 thermal cycle test was performed. They also varied the concentration of $MgCl_2 \cdot 6H_2O$ by 7.0, 10.0 and 15.0 wt% in base material, i.e., $Mg(NO_3)_2 \cdot 6H_2O$. Notable changes in melting point and latent heat of fusion after 1000 cycles were not observed. This material thus could be considered for long-term use as PCM for latent heat storage unit in waste heat recovery.

Tables 6 and 7 show the comparison of melting point, latent heat and thermal cycles of organic and inorganic eutectics, respectively. From the tables, it is observed that the most of the organic and inorganic eutectics which were proposed as PCM were made from fatty acids and salt hydrates, respectively. The thermal stability of most eutectics was confirmed in nearly 1000 or below thermal cycles. As major problems of phase separation and super cooling of salt hydrates, recent researches are more

Table 6
Melting point and latent heat of thermal cycled organic eutectics.

Sr. no.	PCM	Melting point (°C)	Latent heat (J/g)	Thermal cycles	Reference
1.	Ammonium alum ($NH_4Al(SO_4)_2 \cdot 12H_2O$)(15%)+ammonium nitrate (NH_4NO_3)(85%)	53	170	1100	Jotshi et al. [106]
2.	Butyl stearate (49 wt%)+ Butyl palmitate (48 wt%)+other (3 wt%)	17	138	100	Feldman et al. [105]
3.	Capric acid (65 mol%)+lauric acid (35 mol%)	13	116.76	120	Dimaano and Escoto [107]
		19.6	126.5	360	Shilei et al. [110]
4.	Capric acid (73.5 wt%)+myristic acid (26.5 wt%)	21.4	152	5000	Karaipekli et al. [111]
5.	Capric acid (83 wt%)+stearic acid (17 wt%)	24.68	178.64	5000	Karaipekli et al. [87]
6.	Caprylic acid (70 wt%)+1-dodecanol (30 wt%)	6.52	171.06	120	Zuo et al. [113]
7.	Lauric acid (66 wt%)+myristic acid (34 wt%)	34.2	166.8	1460	Sari [109]
8.	Lauric acid (69 wt%)+palmitic acid (31 wt%)	35.2	166.3	1460	Sari [109]
9.	Lauric acid (75.5 wt%)+stearic acid (24.5 wt%) +	37	182.7	360	Sari et al. [108]
10.	Lauric acid (77.05 wt%)+palmitic acid (22.95 wt%)	33.09	150.6	100	Zhang et al. [84]
11.	Methyl stearate (86 wt%)+methyl palmitate (14 wt%)	23.9	220	50	Nikolic et al. [91]
12.	Methyl stearate (91 wt%)+cetyl palmitate (9 wt%)	28.2	189	50	Nikolic et al. [91]
13.	Methyl stearate (91 wt%)+cetyl stearate (9 wt%)	22.2	180	50	Nikolic et al. [91]
14.	Myristic acid (58 wt%)+palmitic acid (42 wt%)	42.6	169.7	360	Sari et al. [108]
15.	Myristic acid (64 wt%)+stearic acid (36 wt%)	44.1	182.4	1460	Sari [109]
16.	Myristic acid+glyserol	31.96	154.3	1000	Sari et al. [112]
17.	Palmitic acid (64.2 wt%)+stearic acid (35.8 wt%)	52.3	181.7	360	Sari et al. [108]
18.	Palmitic acid+glyserol	58.50	185.9	1000	Sari et al. [112]
19.	Stearic acid+glyserol	63.45	149.4	1000	Sari et al. [112]

Table 7
Melting point and latent heat of thermal cycled inorganic eutectics.

Sr. no.	PCM	Melting point (°C)	Latent heat (J/g)	Thermal cycles	Reference
1.	$CaCl_2 \cdot 6H_2O$ (80 mol%)+$CaBr_2 \cdot 6H_2O$ (20 mol%)	20	117	1000	Kimura and Kai [41]
2.	$CaCl_2 \cdot 6H_2O$ (93 wt%)+$Ca(NO_3)_2 \cdot 4H_2O$ (5 wt%)+$Mg(NO_3)_2 \cdot 6H_2O$ (2 wt%)	24	125	1000	Kimura and Kai [41]
3.	$CaCl_2 \cdot 6H_2O$ (96 wt%)+KNO_3 (2 wt%)+KBr (2 wt%)	23	138	1000	Kimura and Kai [41]
4.	$CaCl_2 \cdot 6H_2O$ (96 wt%)+NH_4NO_3 (2 wt%)+NH_4Br (2 wt%)	20	141	1000	Kimura and Kai [41]
5.	$NaCH_3COO \cdot 3H_2O$ (90 wt%)+$NaBr \cdot 2H_2O$ (10 wt%)	51	175	1000	Kimura and Kai [35]
6.	$NaCH_3COO \cdot 3H_2O$ (85 wt%)+$NaHCOO \cdot 3H_2O$ (15 wt%)	49	170	1000	Kimura and Kai [35]
7.	$Mg(NO_3)_2 \cdot 6H_2O$ (93 wt%)+$MgCl_2 \cdot 6H_2O$ (7 wt%)	78	152.4	1000	Nagano et al. [42]

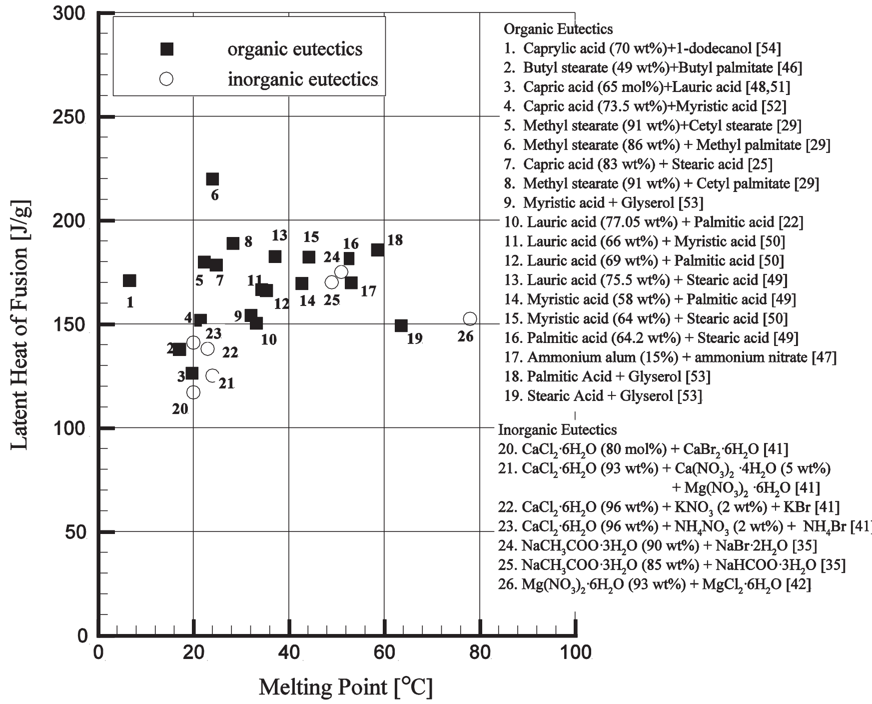


Fig. 4. Latent heat of fusion per unit mass of eutectics undergoing a phase transition within the temperature range 0–100 °C.

focused on organic eutectics. Fig. 4 shows the latent heat of fusion per unit mass of organic and inorganic eutectics undergoing phase transition within a temperature range of 0–80 °C. It can be noted that the melting point of most organic eutectics is in the range of 20–60 °C having latent heat of fusion in the range of 150–200 J/g. Inorganic eutectics made from calcium chloride hexahydrate has melting point near 20 °C and latent heat of fusion below 150 kJ/kg. Methyl stearate (91 wt%)+cetyl palmitate [29] has higher heat of fusion among all eutectics.

4. Summary

A review of thermal stability of phase change materials is prepared based on the survey of literature which reported thermal cycling tests of various PCMs. In this paper, PCMs are categorized as organic (paraffins and non-paraffins), inorganic (salt hydrates and metallics) and eutectics (organic eutectics and inorganic eutectics). The analysis of literature pertaining to the thermal stability of PCMs allows us to draw the following conclusions.

1. The life span of PCM depends on thermal stability, chemical stability and corrosion resistance (containing material compatibility) after number of repeated, consistent thermal cycles. The most thermal stable PCM should have a negligible change in its latent heat and melting point. Hence it is always desirable to ensure thermal stability of PCM for long-term performance of the latent heat storage unit.
2. The most common method used by researchers to establish thermal properties of PCM, i.e., melting point and latent heat of fusion is differential scanning calorimetry (DSC) technique. As accurate information is of vital importance for long-term performance of the storage unit, the effect of the temperature-dependent properties of prospective PCMs like, thermal conductivity, heat capacity and density should also be observed after repeated number of thermal cycles. The chemical stability of PCM after thermal cycling test was evaluated by Fourier transform infrared (FT-IR) spectroscopy. The compatibility of the PCM with the PCM containing materials can also be studied using the scanning electron microscope (SEM).
3. It is found that most organic and inorganic PCMs investigated in the literature are those whose melting temperature is in the range of 30–60 °C and latent heat of fusion is in the range of 150–250 kJ/kg. The most eutectic PCMs studied in literature has the melting point in the range of 20–60 °C and latent heat of fusion is in the range of 125–200 kJ/kg.
4. Most organic PCMs investigated are paraffins and fatty acids. It is found that paraffins have good thermal and chemical stability after number of thermal cycles. The fatty acids studied widely are stearic, lauric, myristic, capric and palmitic acid. Most of the fatty acids used as PCMs are industrial grade. As the thermal behavior of industrial grade PCMs may change, they should be subjected to an accelerated thermal test before the use.
5. Salt hydrates are the most studied Inorganic PCMs. However, phase separation and supercooling is a major problem in salt hydrates. These can be reduced to a certain extent by using gelled or thickened mixtures and using suitable nucleating materials respectively. It is worth to be noted that calcium chloride hexahydrate ($CaCl_2 \cdot 6H_2O$) is the most widely analyzed salt hydrate by many researchers.
6. An eutectic PCM is a combination of two or more compounds which are either organic, inorganic or both. In the last decade, many researchers have shown significant interest in new eutectic type PCMs instead of pure compounds. It is observed that the most of the organic and inorganic eutectics which are proposed as PCMs are made from fatty acids and salt hydrates, respectively.

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